Generalized Holstein model for spin-dependent electron transfer reaction

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Some chemical reactions are described by electron transfer (ET) processes. The underlying mechanism could be modeled as a polaron motion in the molecular crystal—the Holstein model. By taking spin degrees of freedom into consideration, we generalize the Holstein model (molecular crystal model) to microscopically describe an ET chemical reaction. In our model, the electron spins in the radical pair simultaneously interact with a magnetic field and their nuclear-spin environments. By virtue of the perturbation approach, we obtain the chemical reaction rates for different initial states. It is discovered that the chemical reaction rate of the triplet state demonstrates its dependence on the direction of the magnetic field while the counterpart of the singlet state does not. This difference is attributed to the explicit dependence of the triplet state on the direction when the axis is rotated. Our model may provide a possible candidate for the microscopic origin of avian compass.

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I. INTRODUCTION

Nowadays, it has been prevailing in both experimental and theoretical explorations that quantum coherence effect due to the role of phase in quantum superposition may exist in living processes. This essentially implies that there may exist quantum coherence effect in chemical reactions in some living processes, such as charge and energy transfer in photosynthesis [1–5] and singlet-and-triplet transition in avian compass [6–16].

It has long been questioned how migratory birds can navigate to their destination over hundreds of miles. One of the possible answers is given by the radical pair mechanism [9–11]. Two unpaired electron spins in the radical pair are initially prepared in the singlet state. Due to their interactions with the geomagnetic field and their environmental nuclear spins, the election spins coherently transit between the singlet and triplet states. Since the singlet and triplet states could result in different products of chemical reactions, the direction and magnitude of the geomagnetic field determine the relative yields of two distinct products. By sensing the information incorporated in the final products of the chemical reactions in their retinas, the birds can find their way to their destination. Therefore, the quantum coherence underlies in the avian compass since the singlet and triplet spin states correspond to different types of quantum entanglement. Ever since it was proposed a decade ago, the radical-pair-mechanism-based avian compass has been in favor by a series of biological and chemical experiments [6, 7].

In this hypothesis, the nuclear spins play a crucial role because there would be no coherent transition between the singlet and the triplet states if there were no nuclear spins [11]. Previous studies mainly concentrated on the nuclear-spin environment without inter-coupling [13–15].

Mostly recently, by taking into account the inter-coupling of the nuclear spins, we studied a special avian compass model with the nuclear environments modeled by an Ising model in a transverse field [16]. The rationality of this model lies in the fact that the weak inter-nuclear-spin coupling is comparable with the Zeeman energy splitting induced by the weal geomagnetic field. It was discovered that the quantum criticality in the environments enhances the sensitivity of magneto-reception. On the other hand, although various master-equation approaches were proposed to deal with such spin-dependent chemical reactions in the avian compass [7], the underlying physical mechanism is still missing in studying the quantum coherence with microscopic models. Thus, it is urgent to propose appropriate microscopic models for different kinds of chemical reactions to make the quantum coherence effect in those processes better understood. A case in point is the Holstein's molecular crystal model, which is also regarded as a microscopic model of chemical reactions with electron transfer (ET) [17].

The Holstein model was originally proposed to characterize the vibration-assisted ET in one-electron molecular crystal [17]. Here, in order to describe the chemical reaction of spin dependence as well as direction dependence, the Holstein model is generalized to incorporate the degrees of freedom of spin to make electrons naturally interact with a magnetic field. Additionally, due to the presence of the nuclear-spin environments surrounding the electron spins, there would be coherent transition between the singlet and triplet states of the two electron spins. In contrast to the previous investigation using anisotropic hyperfine coupling [11], the hyperfine interaction between the electron spin and its nuclear environment is isotropic in our model. Based on this generalized model, we calculate the chemical reaction rates of the singlet and triplet states of the electron spins. Here, the chemical reaction rate is determined by the transition rate of one electron in a localized molecular orbit to another at a distance. It is discovered that the reaction rate of the triplet state sensitively responses to
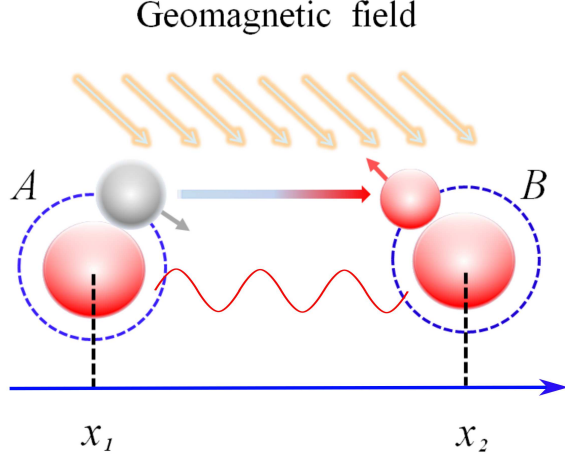
Geomagnetic field

Figure 1: (color online). Schematic diagram for the generalized Holstein model. It is composed of a radical pair with nuclear spins. Two electrons are initially prepared in a correlated state, i.e., the singlet state or triplet state, which can be interconverted by the hyperfine interaction in combination with an external magnetic field. The chemical reaction occurs once both electrons are in the same site due to the tunneling effect.

the variation of the direction of the magnetic field with respect to the polarization of two electron spins. On the contrary, the chemical reaction of the singlet state does not demonstrate such dependence on the direction of the magnetic field. The above results are attributed to the invariance of the singlet state under the rotation of the system around y-axis, while the triplet one will be changed along with the rotation according to irreducible tensor of $SO(3)$ group. Therefore, our proposed model may serve as a microscopic origin for the chemical reaction in the avian compass.

In the next section, we generalize the Holstein model to incorporate the electron spin degrees. In Sec. III, we consider a general case with an external magnetic field and nuclear-spin environments. In Sec. IV, we study the dynamic evolution of the radical pair and obtain the chemical reaction rates for different initial states. Finally, we summarize our main results in the Conclusion. Furthermore, we show the detailed calculations for the chemical reaction probability, the chemical reaction rate and the transition probability from the triplet state to the singlet state in Appendix A and B respectively.

II. GENERALIZED HOLSTEIN MODEL

Many chemical reactions are accompanied by ET, where the electron is transferred from one site to another (Fig. 1). A very important but simple quantum-

mechanical model for ET reactions is the molecular crystal model, which was originally developed by Holstein to describe so-called polaron motion in narrow-band conductors [18] and then understood as a microscopic model in describing simple chemical reactions [17].

The model Hamiltonian $H = H_v + H_e + H_{ev}$ is decomposed into two parts, i.e., the ionic vibration part

$$H_v = \frac{1}{2}\sum_{j=1}^{2}(-\frac{\hbar^2}{m_j}\frac{\partial^2}{\partial x_j^2} + m_j\omega_j^2 x_j^2) + \sqrt{m_1 m_2} f x_1 x_2, \quad (1)$$

and the electron-phonon hybrid part

$$H_e + H_{ev} = \sum_{j,\alpha}\bar{\varepsilon}_j(x_1, x_2)c_{j\alpha}^{\dagger}c_{j\alpha} - J\sum_{\alpha}(c_{1\alpha}^{\dagger}c_{2\alpha} + \text{h.c.}), \quad (2)$$

where x_j is the displacement of the jth ion, ω_j the harmonic vibration frequency with the reduced mass m_j, f the coupling constant of the two molecules, and $c_{j\alpha}(c_{j\alpha}^{\dagger})$ the fermionic annihilation (creation) operator of the electron at molecule j with spin α. Since the orbital energy $\bar{\varepsilon}(x_1, x_2)$ is linearized as

$$\bar{\varepsilon}_j(x_1, x_2) \approx \varepsilon_j + \sum_i \left(\frac{\partial\bar{\varepsilon}_j}{\partial x_i}\right)x_i, \quad (3)$$

we explicitly obtain the electronic Hamiltonian

$$H_e = \sum_{j,\alpha}\varepsilon_j c_{j\alpha}^{\dagger}c_{j\alpha} - J\sum_{\alpha}(c_{1\alpha}^{\dagger}c_{2\alpha} + \text{h.c.}), \quad (4)$$

and the electron-vibration coupling

$$H_{ev} = -\frac{1}{2}\sum_{j,\alpha}A_j c_{j\alpha}^{\dagger}c_{j\alpha}x_j. \quad (5)$$

Here, the molecular orbital energy ε_j is spin-independent. In the next section, we will consider a more general case with an external magnetic field. The tunneling integral J is assumed to be independent of the displacement x_j and $A_j = \sqrt{2}\partial\bar{\varepsilon}_j/\partial x_j$ denotes the electron-vibration coupling, where the term $\partial\bar{\varepsilon}_j/\partial x_i$ for $i \neq j$ is neglected because the molecular orbital energy of the jth molecule changes negligibly when the displacement of the ith molecule varies.

For simplicity, we assume two identical molecules, i.e., $m_1 = m_2 = m$, $\omega_1 = \omega_2$, and $A_1 = A_2 = A$. Choosing coordinates $X = (x_1 + x_2)/\sqrt{2}$ and $x = (x_1 - x_2)/\sqrt{2}$, we decompose the Hamiltonian $H = H_r + H_c$ into two decoupled parts, i.e., the one for the motion of the center of mass

$$H_c = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial X^2} + \frac{1}{2}m\Omega^2 X^2 + AX \quad (6)$$

with $\Omega = \sqrt{\omega_1^2 + f}$, and the other for the relative motion

$$H_r = \hbar\omega(b^\dagger b + \frac{1}{2}) + \sum_{j,\alpha}\varepsilon_j c_{j\alpha}^\dagger c_{j\alpha} - J\sum_\alpha(c_{1\alpha}^\dagger c_{2\alpha} + \text{h.c.}) - \frac{1}{2}A\sqrt{\frac{\hbar}{2m\omega}}(b^\dagger + b)\sum_\alpha(c_{2\alpha}^\dagger c_{2\alpha} - c_{1\alpha}^\dagger c_{1\alpha}), \qquad (7)$$

where we have introduced the bosonic operators

$$b = \sqrt{\frac{m\omega}{2\hbar}}(x + \frac{\hbar}{m\omega}\frac{\partial}{\partial x}), \; b^\dagger = \sqrt{\frac{m\omega}{2\hbar}}(x - \frac{\hbar}{m\omega}\frac{\partial}{\partial x}), \;\; (8)$$

$\omega = \sqrt{\omega_1^2 - f}$ is the effective frequency.

Next, we make the Van Vleck transformation, also called the polaron transformation [19, 20],

$$\check{H} = e^{is}He^{-is} \qquad (9)$$

for the above generalized Holstein model, where

$$s = -i\sum_{j,\alpha}\phi_j(b^\dagger - b)c_{j\alpha}^\dagger c_{j\alpha} \qquad (10)$$

is the transformation kernel and

$$\phi_1 = -\phi_2 = \frac{A}{2\hbar\omega}\sqrt{\frac{\hbar}{2m\omega}} \equiv \phi. \qquad (11)$$

Thus we can formally decouple the degrees of freedom of electron and vibration, obtaining $\check{H}_r = \check{H}_r^{(0)} + \check{H}_r^{(1)}$, with

$$\check{H}_r^{(0)} = \hbar\omega b^\dagger b + \sum_{j\alpha}\varepsilon_j c_{j\alpha}^\dagger c_{j\alpha} - \hbar\omega\left(\sum_{j\alpha}\phi_j c_{j\alpha}^\dagger c_{j\alpha}\right)^2, (12)$$

and

$$\check{H}_r^{(1)} = -J\sum_\alpha(c_{1\alpha}^\dagger c_{2\alpha}e^{2\phi(b^\dagger - b)} + c_{2\alpha}^\dagger c_{1\alpha}e^{-2\phi(b^\dagger - b)}). \;\; (13)$$

This molecular crystal Hamiltonian (12) describes the ET process for a two-local-orbit system. Here, we generalize the Holstein model by taking into consideration the degrees of freedom of the electron spins. Up to now, the above generalization seems to be trivial, since we could totally separate the spin and orbital degrees of freedom. However, when a local external magnetic field is applied to the radical pair to form asymmetric couplings to the two electron spins, the spin-orbit coupling is induced. In this case, a spin-dependent ET process takes place. These asymmetric couplings can also be implemented by coupling to their nuclear-spin environments.

III.   SPIN MOLECULAR CRYSTAL IN MAGNETIC FIELD AND NUCLEAR ENVIRONMENT

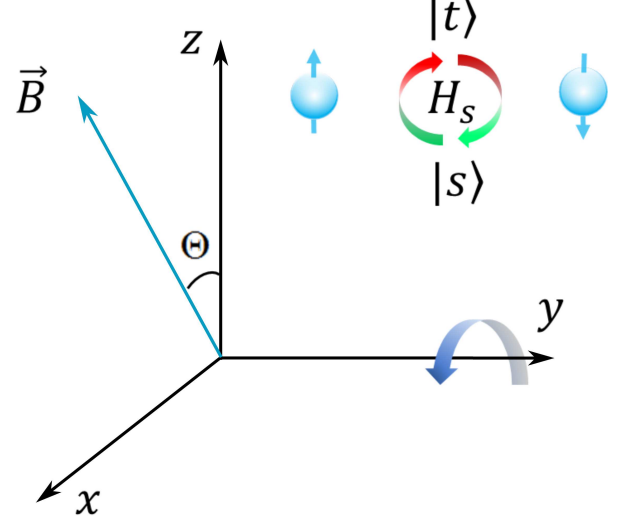In the previous section, we described the generalized Holstein model, with spin degree of freedom. In this

Figure 2: (color online). The inclination angle between the external geomagnetic field and the z-direction is Θ, and the coordinate system is rotated around the y-axis with Θ to coincide with the direction of the the magnetic field. The hyperfine coupling induced interconversion between the singlet and triplet states is modulated by the direction of the magnetic field, i.e., Θ.

section, on account of an external magnetic field and nuclear-spin environments, we investigate how a chemical reaction responses to its magnetic environment.

Choosing the polarization direction of the spin state as the z-direction, we define the singlet state $|s\rangle$ and triplet state $|t\rangle$ of the electron spins as

$$|s\rangle = \frac{1}{\sqrt{2}}(|\uparrow_1^e\downarrow_2^e\rangle - |\downarrow_1^e\uparrow_2^e\rangle) = \frac{1}{\sqrt{2}}\left(c_{1\uparrow}^\dagger c_{2\downarrow}^\dagger - c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger\right)|0\rangle, \;\; (14)$$

and

$$|t\rangle = \frac{1}{\sqrt{2}}(|\uparrow_1^e\downarrow_2^e\rangle + |\downarrow_1^e\uparrow_2^e\rangle) = \frac{1}{\sqrt{2}}\left(c_{1\uparrow}^\dagger c_{2\downarrow}^\dagger + c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger\right)|0\rangle, \;\; (15)$$

respectively with $|0\rangle$ being the vacuum state.

In a simple case where the hyperfine couplings are isotropic, the Hamiltonian, which describes the interaction between the electron spins and their asymmetric magnetic environments (the magnetic field plus the nuclear spins), reads

$$H_s = -\sum_{j=1}^{2}(\mu_B\vec{B}_0 \cdot \hat{S}_j + g_j\hat{I}_j \cdot \hat{S}_j), \qquad (16)$$

where $\vec{B}_0 = B_0(\sin\Theta, 0, \cos\Theta)$ is the external geomagnetic field with the inclination angle Θ, μ_B the Bohr magneton, $\hat{S}_j = (S_j^x, S_j^y, S_j^z)$ the Pauli operators for jth electron spin, $\hat{I}_j = (I_j^x, I_j^y, I_j^z)$ the Pauli operators for jth nuclear spin, and g_j the hyperfine coupling constant between the jth electron spin and its environmental nuclear spin.

Combining the relative vibration and spin Hamiltonians, the total Hamiltonian for a spin-dependent ET reaction is obtained $H_{tot} = H_r + H_s$. After a rotation around y-axis with the angle Θ (Fig. 2), combined with the Van Vleck transformation defined in Eq. (9), we obtain $\tilde{H}_{tot} = \tilde{H}_r + \tilde{H}_s$, where the relative vibration Hamiltonian $\tilde{H}_r = \tilde{H}_r$ is the same as that given in Eqs. (12-13), but the Hamiltonian of the spin part is changed into

$$\tilde{H}_s = -\sum_j (\mu_B B_0 S_{jz} + g_j \hat{I}_j \cdot \hat{S}_j). \qquad (17)$$

Meanwhile, we make the same rotation and transformation for the quantum states of the whole system as in Eq. (9). Straightforwardly, after the combined transformation, the singlet and triplet states read as $|\tilde{s}\rangle = |s\rangle$ and

$$|\tilde{t}\rangle = \cos\Theta |t\rangle + \frac{1}{\sqrt{2}}\sin\Theta(|\uparrow_1^e\uparrow_2^e\rangle - |\downarrow_1^e\downarrow_2^e\rangle), \quad (18)$$

respectively.

It is obvious that the singlet state is not Θ-dependent, while the triplet state is. In the next section, we will study the dependence of chemical reaction rate on the direction of the geomagnetic field. As shown as follows, it is this explicit dependence on the direction in the rotated triplet state that results in the variation of its chemical reaction rate along with the changes of the magnetic field direction.

IV. MAGNETIC DIRECTION CONTROLLING CHEMICAL REACTION

In this section, by means of the perturbation method, we analytically obtain the probability for one electron to transfer to the other local orbit to complete a chemical reaction. Assuming that at the initial time the vibration and nuclear spins are both in thermal equilibrium states and the electron spins are in the triplet state, the density matrix of the whole system $\rho(0) = \rho_v \otimes \rho_n \otimes \rho_t$ includes three parts. The first part

$$\rho_v = \frac{1}{Z}\sum_{m=0}^{\infty}\exp\left(-\frac{m\hbar\omega}{k_B T}\right)|m\rangle\langle m| \qquad (19)$$

denotes the relative vibration of the molecules, where $Z = 1/[1 - \exp(-\hbar\omega/k_B T)]$, k_B the Boltzmann constant, and T the temperature of the environment. The second part is the density matrix of the nuclear spins. Since
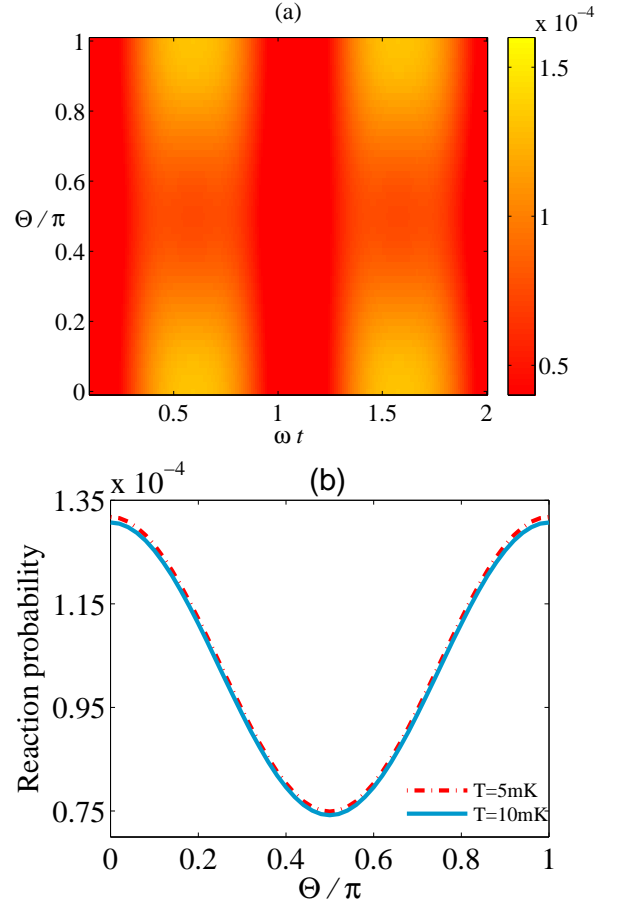

Figure 3: (color online). (a) Chemical reaction probability vs time and Θ. (b) Chemical reaction probability for triplet state at a given time $t = 0.5/\omega$ for effective temperature $T = 5mK$ (red dashed line) and $T = 10mK$ (blue solid line).

$\mu_n B_0 \ll k_B T$ with μ_n the nuclear magneton, the nuclear spins are in the state

$$\rho_n = \frac{1}{4}\sum_{j=1}^{4}|\chi_j^n\rangle\langle\chi_j^n|, \qquad (20)$$

where $|\chi_1^n\rangle = |\downarrow_1^n\downarrow_2^n\rangle$, $|\chi_2^n\rangle = |\downarrow_1^n\uparrow_2^n\rangle$, $|\chi_3^n\rangle = |\uparrow_1^n\downarrow_2^n\rangle$, and $|\chi_4^n\rangle = |\uparrow_1^n\uparrow_2^n\rangle$. The last one

$$\rho_t = |t\rangle\langle t| \qquad (21)$$

describes the electrons.

Starting from the above initial state, we calculate the total ET reaction probability of the triplet state (for the details please refer to Appendix A)

$$P_t(\tau) = \frac{1}{4Z}\sum_{m,n=0}^{\infty}\sum_{j=1}^{4}\sum_{p=1}^{24}e^{-\beta m\hbar\omega}P_{jmnp}(\tau), \qquad (22)$$

where

$$P_{jmnp}(\tau) = \left|\sum_q c_{jmq}\tilde{H}_{np,mq}^{(1)}\frac{1 - e^{i\omega_{np,mq}\tau}}{\hbar\omega_{np,mq}}\right|^2, \qquad (23)$$

and $c_{jmq} = \langle \psi_{mq}^{(0)} | \tilde{t} \rangle | \chi_j^n \rangle | m \rangle$ is the expanding coefficient. And the chemical reaction rate is determined by the reaction probability per unite time in the long-time limit [21]

$$k_t = \frac{\partial}{\partial \tau} \lim_{\tau \to \infty} P_t(\tau), \qquad (24)$$

where the explicit expression which displays direction dependence is given in Appendix A.

To show the above results in an intuitive way, we turn to numerical examples. We take the orbital energy difference $\Delta = \varepsilon_1 - \varepsilon_2 = 0.01$eV and the relative vibration frequency $\omega = 10^7$Hz. We assume the tunneling integral $J = 0.01\Delta$ and $\phi = 0.2$. The magnitude of the geomagnetic field is $B_0 = 50\mu$T and the hyperfine coupling constant is $g_1 = g_2 = 10^{-8}$eV. In the following calculations, we need to take a cut of the phonon occupation number, defined by an effective temperature of the environment. We find that the chemical reaction probability is not sensitive to the temperature of the environment. For these parameters we numerically calculate the transition probability for initial triplet state from Eq. (22) as shown in Fig. 3.

Obviously, the ET probability displays its dependence on the angle Θ. At a given time, the ET probability falls to its minimum value when the magnetic field is perpendicular to z direction, while it reaches its maximum when the direction of the external field is parallel to z axis. Besides, the probability is symmetrical about $\Theta = \pi/2$. When we come to the initial singlet state, there is no such dependence on the angle Θ. This is a reasonable result for isotropic hyperfine coupling case since both the singlet state and the transformed Hamiltonian do not explicitly depend on the angle.

On the other hand, the chemical reaction rate for triplet state would vanish once there were no interaction between the electron spins and their nuclear environments, i.e., $g_j = 0$, while the ET reaction happens when the electron spins are in the singlet state. This can be seen from the fact that $H_r^{(1)}|t\rangle = 0$ but $H_r^{(1)}|s\rangle \neq 0$. The coupling of electron spins to the nuclear-spin environments can induce the transition from the triplet to the singlet states to make the ET happen. Then the spatial ET leads to the chemical reaction. In order to illustrate the mechanism of magnetic-direction-controlling chemical reaction more clearly, we study the dynamic evolution of the radical pair. Using the same parameters as those in Fig. 3, we plot the transition probability from the triplet state to the singlet state

$$P_{t \to s} = \text{Tr}_{v,n,e} \left[\tilde{\rho}_s e^{-i\tilde{H}t/\hbar} \tilde{\rho}(0) e^{i\tilde{H}t/\hbar} \right] \qquad (25)$$

in Fig. 4. Due to the presence of the nuclear-spin environments, there is periodical interconversion between the singlet and triplet states. Besides, the amplitude of this periodical oscillation is adjusted by the direction of the magnetic field. For one thing, the singlet-triplet interconversion is induced by the hyperfine couplings, not the uniform magnetic field, but it is modulated by the
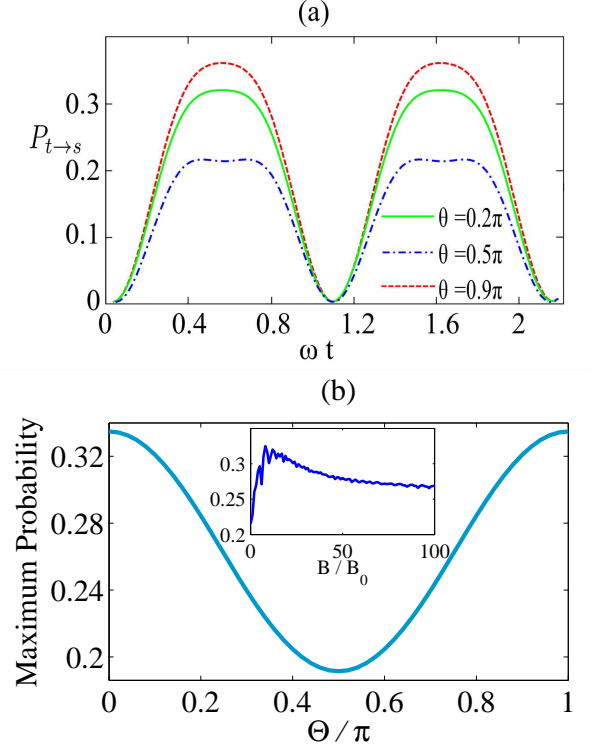

Figure 4: (color online). Transition probability from the triplet state to singlet state. (a) Probability vs time for different angles. (b) The maximum probability varies with angle. The inset displays that the maximum transition probability also changes with the magnitude of the magnetic field.

geomagnetic field. Our conjecture, that the triplet state is converted to the singlet state to complete the ET reaction, is confirmed by the same line shape of the maximum conversion probability as that of the chemical reaction probability of the triplet state. Besides, as shown in the inset of Fig. 4(b), with the increasing of the magnitude of the magnetic field, the maximum of the transition probability increase at first for a given angle $\Theta = 0.1\pi$ and finally decreases into a stable value.

V. CONCLUSION

On account of electron spin degrees of freedom, we study the effect of the direction of the magnetic field on the chemical reaction by generalizing the Holstein model. By means of the perturbation approach, we obtain the ET reaction probability and chemical reaction rate of the singlet and triplet states. The chemical reaction rate of the triplet state displays its sensitive dependence on the direction of the magnetic field in contrast to the counterpart of the singlet state. We demonstrate that the triplet state indirectly participates in the chemical reaction. It must be converted to the singlet state by the hyperfine coupling between electrons and nuclear spins to take part in the ET reaction. We emphasize that the hyperfine cou-

plings are isotropic in our model which are different from the anisotropic ones in the previous study [11]. With the above comprehensive consideration, it could be concluded that our model may serve as a possible microscopic origin for the avian compass.

Appendix A: Chemical reaction rate

In this appendix, we calculate the ET reaction probability to the first order.

First of all, the Hamiltonian of the electron spin-j part $\tilde{H}_s^{(j)}$ is diagonalized with eigenstates

$$\left|e_1^{(j)}\right\rangle = \left|\downarrow_j^e\right\rangle \left|\downarrow_j^n\right\rangle, \tag{A1}$$

$$\left|e_2^{(j)}\right\rangle = \cos\frac{\theta_j}{2}\left|\downarrow_j^e\right\rangle\left|\uparrow_j^n\right\rangle - \sin\frac{\theta_j}{2}\left|\uparrow_j^e\right\rangle\left|\downarrow_j^n\right\rangle, \tag{A2}$$

$$\left|e_3^{(j)}\right\rangle = \sin\frac{\theta_j}{2}\left|\downarrow_j^e\right\rangle\left|\uparrow_j^n\right\rangle + \cos\frac{\theta_j}{2}\left|\uparrow_j^e\right\rangle\left|\downarrow_j^n\right\rangle, \tag{A3}$$

$$\left|e_4^{(j)}\right\rangle = \left|\uparrow_j^e\right\rangle\left|\uparrow_j^n\right\rangle, \tag{A4}$$

and the corresponding eigenvalues

$$e_1^{(j)} = \mu_B B_0 - g_j, \tag{A5}$$
$$e_2^{(j)} = g_j + \sqrt{\mu_B^2 B_0^2 + 4g_j^2}, \tag{A6}$$
$$e_3^{(j)} = g_j - \sqrt{\mu_B^2 B_0^2 + 4g_j^2}, \tag{A7}$$
$$e_4^{(j)} = -\mu_B B_0 - g_j. \tag{A8}$$

Here, the mixing angles is defined as

$$\theta_j = \tan^{-1}\left(\frac{2g_j}{\mu_B B_0}\right). \tag{A9}$$

Straightforwardly, we explicitly calculate the eigenstates and eigenvalues of the total Hamiltonian for the spins $\tilde{H}_s = \sum_j \tilde{H}_s^{(j)}$, listed in Table I.

The total Hamiltonian $\tilde{H} = \tilde{H}^{(0)} + \tilde{H}^{(1)}$ is split into two parts, i.e., $\tilde{H}^{(0)} = \tilde{H}_r^{(0)} + \tilde{H}_s$ governing the free dynamic evolution and $\tilde{H}^{(1)} = \tilde{H}_r^{(1)}$ for the ET process. $|\psi_{mq}^{(0)}\rangle = |\varphi_q\rangle \otimes |m\rangle$ are the eigenstates of $\tilde{H}^{(0)}$ with eigenvalues

Eigenstate	Eigenvalue
$\|\varphi_1\rangle = \|e_1^{(1)}\rangle \otimes \|e_1^{(2)}\rangle$	$E_{s1} = e_1^{(1)} + e_1^{(2)}$
$\|\varphi_2\rangle = \|e_1^{(1)}\rangle \otimes \|e_2^{(2)}\rangle$	$E_{s2} = e_1^{(1)} + e_2^{(2)}$
$\|\varphi_3\rangle = \|e_1^{(1)}\rangle \otimes \|e_3^{(2)}\rangle$	$E_{s3} = e_1^{(1)} + e_3^{(2)}$
$\|\varphi_4\rangle = \|e_1^{(1)}\rangle \otimes \|e_4^{(2)}\rangle$	$E_{s4} = e_1^{(1)} + e_4^{(2)}$
$\|\varphi_5\rangle = \|e_2^{(1)}\rangle \otimes \|e_1^{(2)}\rangle$	$E_{s5} = e_2^{(1)} + e_1^{(2)}$
$\|\varphi_6\rangle = \|e_2^{(1)}\rangle \otimes \|e_2^{(2)}\rangle$	$E_{s6} = e_2^{(1)} + e_2^{(2)}$
$\|\varphi_7\rangle = \|e_2^{(1)}\rangle \otimes \|e_3^{(2)}\rangle$	$E_{s7} = e_2^{(1)} + e_3^{(2)}$
$\|\varphi_8\rangle = \|e_2^{(1)}\rangle \otimes \|e_4^{(2)}\rangle$	$E_{s8} = e_2^{(1)} + e_4^{(2)}$
$\|\varphi_9\rangle = \|e_3^{(1)}\rangle \otimes \|e_1^{(2)}\rangle$	$E_{s9} = e_3^{(1)} + e_1^{(2)}$
$\|\varphi_{10}\rangle = \|e_3^{(1)}\rangle \otimes \|e_2^{(2)}\rangle$	$E_{s10} = e_3^{(1)} + e_2^{(2)}$
$\|\varphi_{11}\rangle = \|e_3^{(1)}\rangle \otimes \|e_3^{(2)}\rangle$	$E_{s11} = e_3^{(1)} + e_3^{(2)}$
$\|\varphi_{12}\rangle = \|e_3^{(1)}\rangle \otimes \|e_4^{(2)}\rangle$	$E_{s12} = e_3^{(1)} + e_4^{(2)}$
$\|\varphi_{13}\rangle = \|e_4^{(1)}\rangle \otimes \|e_1^{(2)}\rangle$	$E_{s13} = e_4^{(1)} + e_1^{(2)}$
$\|\varphi_{14}\rangle = \|e_4^{(1)}\rangle \otimes \|e_2^{(2)}\rangle$	$E_{s14} = e_4^{(1)} + e_2^{(2)}$
$\|\varphi_{15}\rangle = \|e_4^{(1)}\rangle \otimes \|e_3^{(2)}\rangle$	$E_{s15} = e_4^{(1)} + e_3^{(2)}$
$\|\varphi_{16}\rangle = \|e_4^{(1)}\rangle \otimes \|e_4^{(2)}\rangle$	$E_{s16} = e_4^{(1)} + e_4^{(2)}$
$\|\varphi_{17}\rangle = \|\uparrow_1^e\downarrow_1^e\rangle \otimes \|\downarrow_1^n\downarrow_2^n\rangle$	$E_{s17} = 0$
$\|\varphi_{18}\rangle = \|\uparrow_1^e\downarrow_1^e\rangle \otimes \|\downarrow_1^n\uparrow_2^n\rangle$	$E_{s18} = 0$
$\|\varphi_{19}\rangle = \|\uparrow_1^e\downarrow_1^e\rangle \otimes \|\uparrow_1^n\downarrow_2^n\rangle$	$E_{s19} = 0$
$\|\varphi_{20}\rangle = \|\uparrow_1^e\downarrow_1^e\rangle \otimes \|\uparrow_1^n\uparrow_2^n\rangle$	$E_{s20} = 0$
$\|\varphi_{21}\rangle = \|\uparrow_2^e\downarrow_2^e\rangle \otimes \|\downarrow_1^n\downarrow_2^n\rangle$	$E_{s21} = 0$
$\|\varphi_{22}\rangle = \|\uparrow_2^e\downarrow_2^e\rangle \otimes \|\downarrow_1^n\uparrow_2^n\rangle$	$E_{s21} = 0$
$\|\varphi_{23}\rangle = \|\uparrow_2^e\downarrow_2^e\rangle \otimes \|\uparrow_1^n\downarrow_2^n\rangle$	$E_{s22} = 0$
$\|\varphi_{24}\rangle = \|\uparrow_2^e\downarrow_2^e\rangle \otimes \|\uparrow_1^n\uparrow_2^n\rangle$	$E_{s24} = 0$

Table I: All 24 eigenstates and eigenvalues of $\tilde{H}_s$, where the two electrons are located in two distant orbits respectively for the first 16 eigenstates, while for the other 8 eigenstates, both electrons are in the same site.

$E_{mq}^{(0)} = m\hbar\omega + E_{sq}$. Here, m ($m = 0, ..., \infty$) denotes the relative vibrational quantum number. A given initial state is expanded as

$$|\Psi_m(0)\rangle = \sum_{q=1}^{24} c_{mq}(0)|\psi_{mq}^{(0)}\rangle, \tag{A10}$$

and then the wave function at time t is given by

$$|\Psi(t)\rangle = \sum_{n=0}^{\infty}\sum_{p=1}^{24} c_{np}(t)\exp[-iE_{np}^{(0)}t/\hbar]|\psi_{np}^{(0)}\rangle, \tag{A11}$$

where $c_{np}(t)$ are the coefficients determined by the Schrödinger equation

$$i\hbar\dot{c}_{np}(t) = \sum_{n',p'} e^{i\omega_{np,n'p'}t}\tilde{H}_{np,n'p'}^{(1)}c_{n',p'}(t). \tag{A12}$$

Here,

$$\omega_{np,n'p'} = [E_{np}^{(0)} - E_{n'p'}^{(0)}]/\hbar, \tag{A13}$$

Coefficient	Explicit expression
$R_{1,mn,21}$	$\cos^2\Theta[\sin^2\frac{\theta_2}{2}\sin^2\frac{\theta_2}{2}\delta\left(E_{n,21}^{(0)}-E_{m,2}^{(0)}\right)+\cos^2\frac{\theta_2}{2}\cos^2\frac{\theta_2}{2}\delta\left(E_{n,21}^{(0)}-E_{m,3}^{(0)}\right)$ $+\sin^2\frac{\theta_1}{2}\sin^2\frac{\theta_1}{2}\delta\left(E_{n,21}^{(0)}-E_{m,5}^{(0)}\right)+\cos^2\frac{\theta_1}{2}\cos^2\frac{\theta_1}{2}\delta\left(E_{n,21}^{(0)}-E_{m,9}^{(0)}\right)]$
$R_{1,mn,22}$	$\frac{1}{4}\sin^2\Theta[\sin^4\frac{\theta_1}{2}\sin^2\theta_2\delta\left(E_{n,22}^{(0)}-E_{m,6}^{(0)}\right)+\sin^4\frac{\theta_1}{2}\sin^2\theta_2\delta\left(E_{n,22}^{(0)}-E_{m,7}^{(0)}\right)$ $+\cos^4\frac{\theta_1}{2}\sin^2\theta_2\delta\left(E_{n,22}^{(0)}-E_{m,10}^{(0)}\right)+\cos^4\frac{\theta_1}{2}\sin^2\theta_2\delta\left(E_{n,22}^{(0)}-E_{m,11}^{(0)}\right)]$
$R_{1,mn,23}$	$\frac{1}{4}\sin^2\Theta[\sin^2\theta_1\sin^4\frac{\theta_2}{2}\delta\left(E_{n,23}^{(0)}-E_{m,6}^{(0)}\right)+\sin^2\theta_1\cos^4\frac{\theta_2}{2}\delta\left(E_{n,23}^{(0)}-E_{m,7}^{(0)}\right)$ $+\sin^2\theta_1\sin^4\frac{\theta_2}{2}\delta\left(E_{n,23}^{(0)}-E_{m,10}^{(0)}\right)+\sin^2\theta_1\cos^4\frac{\theta_2}{2}\delta\left(E_{n,23}^{(0)}-E_{m,11}^{(0)}\right)]$
$R_{1,mn,24}$	0
$R_{2,mn,21}$	$\sin^2\Theta[\cos^2\frac{\theta_2}{2}\sin^2\frac{\theta_2}{2}\delta\left(E_{n,21}^{(0)}-E_{m,2}^{(0)}\right)+\sin^2\frac{\theta_2}{2}\cos^2\frac{\theta_2}{2}\delta\left(E_{n,21}^{(0)}-E_{m,3}^{(0)}\right)]$
$R_{2,mn,22}$	$\cos^2\Theta[\delta\left(E_{n,22}^{(0)}-E_{m,4}^{(0)}\right)+\sin^4\frac{\theta_1}{2}\cos^4\frac{\theta_2}{2}\delta\left(E_{n,22}^{(0)}-E_{m,6}^{(0)}\right)+\sin^4\frac{\theta_1}{2}\sin^4\frac{\theta_2}{2}\delta\left(E_{n,22}^{(0)}-E_{m,7}^{(0)}\right)$ $+\cos^4\frac{\theta_1}{2}\cos^4\frac{\theta_2}{2}\delta\left(E_{n,22}^{(0)}-E_{m,10}^{(0)}\right)+\cos^4\frac{\theta_1}{2}\sin^4\frac{\theta_2}{2}\delta\left(E_{n,22}^{(0)}-E_{m,11}^{(0)}\right)]$
$R_{2,nm,23}$	$\frac{1}{16}\cos^2\Theta[\sin^2\theta_1\sin^2\theta_2\delta\left(E_{n,23}^{(0)}-E_{m,6}^{(0)}\right)+\sin^2\theta_1\sin^2\theta_2\delta\left(E_{n,23}^{(0)}-E_{m,7}^{(0)}\right)$ $+\sin^2\theta_1\sin^2\theta_2\delta\left(E_{n,23}^{(0)}-E_{m,10}^{(0)}\right)+\sin^2\theta_1\sin^2\theta_2\delta\left(E_{n,23}^{(0)}-E_{m,11}^{(0)}\right)]$
$R_{2,nm,24}$	$\sin^2\Theta[\sin^2\frac{\theta_1}{2}\cos^2\frac{\theta_1}{2}\delta\left(E_{n,24}^{(0)}-E_{m,8}^{(0)}\right)+\cos^2\frac{\theta_1}{2}\sin^2\frac{\theta_1}{2}\delta\left(E_{n,24}^{(0)}-E_{m,12}^{(0)}\right)]$
$R_{3,mn,21}$	$\sin^2\Theta[\sin^2\frac{\theta_1}{2}\cos^2\frac{\theta_1}{2}\delta\left(E_{n,21}^{(0)}-E_{m,5}^{(0)}\right)+\sin^2\frac{\theta_1}{2}\cos^2\frac{\theta_1}{2}\delta\left(E_{n,21}^{(0)}-E_{m,9}^{(0)}\right)]$
$R_{3,mn,22}$	$\frac{1}{16}\cos^2\Theta[\sin^2\theta_1\sin^2\theta_2\delta\left(E_{n,22}^{(0)}-E_{m,6}^{(0)}\right)+\sin^2\theta_1\sin^2\theta_2\delta\left(E_{n,22}^{(0)}-E_{m,7}^{(0)}\right)$ $+\sin^2\theta_1\sin^2\theta_2\delta\left(E_{n,22}^{(0)}-E_{m,10}^{(0)}\right)+\sin^2\theta_1\sin^2\theta_2\delta\left(E_{n,22}^{(0)}-E_{m,11}^{(0)}\right)]$
$R_{3,mn,23}$	$\cos^2\Theta[\delta\left(E_{n,23}^{(0)}-E_{m,11}^{(0)}\right)+\cos^4\frac{\theta_1}{2}\sin^4\frac{\theta_2}{2}\delta\left(E_{n,23}^{(0)}-E_{m,6}^{(0)}\right)+\cos^4\frac{\theta_1}{2}\cos^4\frac{\theta_2}{2}\delta\left(E_{n,23}^{(0)}-E_{m,7}^{(0)}\right)$ $+\sin^4\frac{\theta_1}{2}\sin^4\frac{\theta_2}{2}\delta\left(E_{n,23}^{(0)}-E_{m,10}^{(0)}\right)+\sin^4\frac{\theta_1}{2}\cos^4\frac{\theta_2}{2}\delta\left(E_{n,23}^{(0)}-E_{m,11}^{(0)}\right)]$
$R_{3,mn,24}$	$\sin^2\Theta[\sin^2\frac{\theta_2}{2}\cos^2\frac{\theta_2}{2}\delta\left(E_{n,24}^{(0)}-E_{m,14}^{(0)}\right)+\sin^2\frac{\theta_2}{2}\cos^2\frac{\theta_2}{2}\delta\left(E_{n,24}^{(0)}-E_{m,15}^{(0)}\right)]$
$R_{4,mn,21}$	0
$R_{4,mn,22}$	$\frac{\sin^2\Theta}{4}[\sin^2\theta_1\cos^4\frac{\theta_2}{2}\delta\left(E_{n,22}^{(0)}-E_{m,6}^{(0)}\right)+\sin^2\theta_1\sin^4\frac{\theta_2}{2}\delta\left(E_{n,22}^{(0)}-E_{m,7}^{(0)}\right)$ $+\sin^2\theta_1\cos^4\frac{\theta_2}{2}\delta\left(E_{n,22}^{(0)}-E_{m,10}^{(0)}\right)+\sin^2\theta_1\cos^2\frac{\theta_2}{2}\delta\left(E_{n,22}^{(0)}-E_{m,11}^{(0)}\right)]$
$R_{4,mn,23}$	$\frac{\sin^2\Theta}{4}[\cos^4\frac{\theta_1}{2}\sin^2\theta_2\delta\left(E_{n,23}^{(0)}-E_{m,6}^{(0)}\right)+\cos^4\frac{\theta_1}{2}\sin^2\theta_2\delta\left(E_{n,23}^{(0)}-E_{m,7}^{(0)}\right)$ $+\sin^4\frac{\theta_1}{2}\sin^2\theta_2\delta\left(E_{n,23}^{(0)}-E_{m,10}^{(0)}\right)+\sin^4\frac{\theta_1}{2}\sin^2\theta_2\delta\left(E_{n,23}^{(0)}-E_{m,11}^{(0)}\right)]$
$R_{4,mn,24}$	$\cos^2\Theta[\cos^4\frac{\theta_1}{2}\delta\left(E_{n,24}^{(0)}-E_{m,8}^{(0)}\right)+\sin^4\frac{\theta_1}{2}\delta\left(E_{n,24}^{(0)}-E_{m,11}^{(0)}\right)$ $+\cos^4\frac{\theta_2}{2}\delta\left(E_{n,24}^{(0)}-E_{m,14}^{(0)}\right)+\sin^2\frac{\theta_2}{2}\delta\left(E_{n,24}^{(0)}-E_{m,15}^{(0)}\right)]$

Table II: Coefficients for the chemical reaction rate of the triplet state.

and

$$\tilde{H}_{np,n'p'}^{(1)} = \langle\psi_{np}^{(0)}|H^{(1)}|\psi_{n'p'}^{(0)}\rangle. \tag{A14}$$

To the first-order approximation, as $c_{n'p'}(t)$ in the right-hand side of Eq. (A12) is approximated as $c_{mp'}(0)\delta_{n',m}$, it is straightforward to obtain

$$c_{np}(\tau) = c_{np}(0) - \sum_q c_{mq}(0)\tilde{H}_{np,mq}^{(1)}\frac{e^{i\omega_{np,mq}\tau}-1}{\hbar\omega_{np,mq}}. \tag{A15}$$

The square of its norm gives the probability P_{np} of finding the system in the state $|\psi_{np}^{(0)}\rangle$ at time τ. Thus, for $(n,p)\neq$ (m,q), we have

$$P_{np}(\tau) = \left|\sum_q c_{mq}(0)\tilde{H}_{np,mq}^{(1)}\frac{e^{i\omega_{np,mq}\tau}-1}{\hbar\omega_{np,mq}}\right|^2. \tag{A16}$$

The total ET reaction probability is $P(\tau)=\sum_{np}P_{np}(\tau)$. And the chemical reaction rate is determined by the reaction probability per unit time in the long-time limit [21], i.e.,

$$k = \frac{\partial}{\partial\tau}\lim_{\tau\to\infty}P(\tau). \tag{A17}$$

In our case, the system is initially in the state $\rho(0) = \rho_v\otimes\rho_n\otimes\rho_t$, i.e., the relative vibration part

$$\rho_v = \frac{1}{Z}\sum_{m=0}^{\infty}e^{-\beta m\hbar\omega}|m\rangle\langle m|, \tag{A18}$$

Coefficient	Explicit expression
$D_{m,1,1}$	$\frac{1}{2}[-\sin\frac{\theta_2}{2}\sin\frac{\theta_2}{2}\cos\Theta e^{-iE_{m,2}t/\hbar} - \cos\frac{\theta_2}{2}\cos\frac{\theta_2}{2}\cos\Theta e^{-iE_{m,3}t/\hbar}$ $+ \sin\frac{\theta_1}{2}\sin\frac{\theta_1}{2}\cos\Theta e^{-iE_{m,5}t/\hbar} + \cos\frac{\theta_1}{2}\cos\frac{\theta_1}{2}\cos\Theta e^{-iE_{m,9}t/\hbar}]$
$D_{m,1,2}$	$\frac{1}{4}[-\sin^2\frac{\theta_1}{2}\sin\theta_2\sin\Theta e^{-iE_{m,6}t/\hbar} + \sin^2\frac{\theta_1}{2}\sin\theta_2\sin\Theta e^{-iE_{m,7}t/\hbar}$ $- \cos^2\frac{\theta_1}{2}\sin\theta_2\sin\Theta e^{-iE_{m,10}t/\hbar} + \cos^2\frac{\theta_1}{2}\sin\theta_2\sin\Theta e^{-iE_{m,11}t/\hbar}]$
$D_{m,1,3}$	$\frac{1}{4}[\sin\theta_1\sin^2\frac{\theta_2}{2}\sin\Theta e^{-iE_{m,6}t/\hbar} + \sin\theta_1\cos^2\frac{\theta_2}{2}\sin\Theta e^{-iE_{m,7}t/\hbar}$ $- \sin\theta_1\sin^2\frac{\theta_2}{2}\sin\Theta e^{-iE_{m,10}t/\hbar} - \sin\theta_1\cos^2\frac{\theta_2}{2}\sin\Theta e^{-iE_{m,11}t/\hbar}]$
$D_{m,1,4}$	0
$D_{m,2,1}$	$\frac{1}{2}[-\sin\frac{\theta_2}{2}\cos\frac{\theta_2}{2}\sin\Theta e^{-iE_{m,2}t/\hbar} + \cos\frac{\theta_2}{2}\sin\frac{\theta_2}{2}\sin\Theta e^{-iE_{m,3}t/\hbar}]$
$D_{m,2,2}$	$\frac{1}{2}[-\cos\Theta e^{-iE_{m,4}t/\hbar} + \sin^2\frac{\theta_1}{2}\cos^2\frac{\theta_2}{2}\cos\Theta e^{-iE_{m,6}t/\hbar} + \sin^2\frac{\theta_1}{2}\sin^2\frac{\theta_2}{2}\cos\Theta e^{-iE_{m,7}t/\hbar}$ $+ \cos^2\frac{\theta_1}{2}\cos^2\frac{\theta_2}{2}\cos\Theta e^{-iE_{m,10}t/\hbar} + \cos^2\frac{\theta_1}{2}\sin^2\frac{\theta_2}{2}\cos\Theta e^{-iE_{m,11}t/\hbar}]$
$D_{m,2,3}$	$\frac{1}{8}[-\sin\theta_1\sin\theta_2\cos\Theta e^{-iE_{m,6}t/\hbar} + \sin\theta_1\sin\theta_2\cos\Theta e^{-iE_{m,7}t/\hbar}$ $+ \sin\theta_1\sin\theta_2\cos\Theta e^{-iE_{m,10}t/\hbar} - \sin\theta_1\sin\theta_2\cos\Theta e^{-iE_{m,11}t/\hbar}]$
$D_{m,2,4}$	$\frac{1}{2}[\cos\frac{\theta_1}{2}\sin\frac{\theta_1}{2}\sin\Theta e^{-iE_{m,8}t/\hbar} - \sin\frac{\theta_1}{2}\cos\frac{\theta_1}{2}\sin\Theta e^{-iE_{m,12}t/\hbar}]$
$D_{m,3,1}$	$\frac{1}{2}[\sin\frac{\theta_1}{2}\cos\frac{\theta_1}{2}\sin\Theta e^{-iE_{m,5}t/\hbar} - \cos\frac{\theta_1}{2}\sin\frac{\theta_1}{2}\sin\Theta e^{-iE_{m,9}t/\hbar}]$
$D_{m,3,2}$	$\frac{1}{8}[\sin\theta_1\sin\theta_2\cos\Theta e^{-iE_{m,6}t/\hbar} - \sin\theta_1\sin\theta_2\cos\Theta e^{-iE_{m,7}t/\hbar}$ $- \sin\theta_1\sin\theta_2\cos\Theta e^{-iE_{m,10}t/\hbar} + \sin\theta_1\sin\theta_2\cos\Theta e^{-iE_{m,11}t/\hbar}]$
$D_{m,3,3}$	$\frac{1}{2}[-\cos^2\frac{\theta_1}{2}\sin^2\frac{\theta_2}{2}\cos\Theta e^{-iE_{m,6}t/\hbar} - \cos^2\frac{\theta_1}{2}\cos^2\frac{\theta_2}{2}\cos\Theta e^{-iE_{m,7}t/\hbar}$ $- \sin^2\frac{\theta_1}{2}\sin^2\frac{\theta_2}{2}\cos\Theta e^{-iE_{m,10}(\varphi_{10})t/\hbar} - \sin^2\frac{\theta_1}{2}\cos^2\frac{\theta_2}{2}\cos\Theta e^{-iE_{m,11}t/\hbar} + \cos\Theta e^{-iE_{m,13}t/\hbar}]$
$D_{m,3,4}$	$\frac{1}{2}[-\cos\frac{\theta_2}{2}\sin\frac{\theta_2}{2}\sin\Theta e^{-iE_{m,14}(\varphi_{14})t/\hbar} + \sin\frac{\theta_2}{2}\cos\frac{\theta_2}{2}\sin\Theta e^{-iE_{m,15}(\varphi_{15})t/\hbar}]$
$D_{m,4,1}$	0
$D_{m,4,2}$	$\frac{1}{4}[\sin\theta_1\cos^2\frac{\theta_2}{2}\sin\Theta e^{-iE_{m,6}t/\hbar} + \sin\theta_1\sin^2\frac{\theta_2}{2}\sin\Theta e^{-iE_{m,7}t/\hbar}$ $- \sin\theta_1\cos^2\frac{\theta_2}{2}\sin\Theta e^{-iE_{m,10}t/\hbar} - \sin\theta_1\sin^2\frac{\theta_2}{2}\sin\Theta e^{-iE_{m,11}t/\hbar}]$
$D_{m,4,3}$	$\frac{1}{4}[-\cos^2\frac{\theta_1}{2}\sin\theta_2\sin\Theta e^{-iE_{m,6}t/\hbar} + \cos^2\frac{\theta_1}{2}\sin\theta_2\sin\Theta e^{-iE_{m,7}t/\hbar}$ $- \sin^2\frac{\theta_1}{2}\sin\theta_2\sin\Theta e^{-iE_{m,10}t/\hbar} + \sin^2\frac{\theta_1}{2}\sin\theta_2\sin\Theta e^{-iE_{m,11}t/\hbar}]$
$D_{m,4,4}$	$\frac{1}{2}[-\cos\frac{\theta_1}{2}\cos\frac{\theta_1}{2}\cos\Theta e^{-iE_{m,8}t/\hbar} - \sin\frac{\theta_1}{2}\sin\frac{\theta_1}{2}\cos\Theta e^{-iE_{m,12}t/\hbar}$ $+ \cos\frac{\theta_2}{2}\cos\frac{\theta_2}{2}\cos\Theta e^{-iE_{m,14}t/\hbar} + \sin\frac{\theta_2}{2}\sin\frac{\theta_2}{2}\cos\Theta e^{-iE_{m,15}t/\hbar}]$

Table III: Coefficients for the probability from the triplet to the singlet state at time t.

with

$$Z = 1/[1 - \exp(-\hbar\omega/k_B T)], \qquad (A19)$$

the nuclear spin part

$$\rho_n = \frac{1}{4}\sum_{j=1}^{4}\left|\chi_j^n\right\rangle\left\langle\chi_j^n\right|, \qquad (A20)$$

and the electron spin part

$$\rho_t = |t\rangle\langle t|. \qquad (A21)$$

After the Van Vleck transformation (9) and the rotation for the system, the initial state is transformed as $\tilde{\rho}(0) = \tilde{\rho}_v \otimes \tilde{\rho}_n \otimes \tilde{\rho}_t$, where $\tilde{\rho}_v = \rho_v$, $\tilde{\rho}_n = \rho_n$, and $\tilde{\rho}_t = |\tilde{t}\rangle\langle\tilde{t}|$. And we calculate the total chemical reaction probability as

$$P_t(\tau) = \frac{1}{4Z}\sum_{m,n=0}^{\infty}\sum_{j=1}^{4}\sum_{p=1}^{24} e^{-\beta m\hbar\omega} P_{jmnp}(\tau), \qquad (A22)$$

where

$$P_{jmnp}(\tau) = \left|\sum_q c_{jmq}\tilde{H}_{np,mq}^{(1)}\frac{1 - e^{i\omega_{np,mq}\tau}}{\hbar\omega_{np,mq}}\right|^2, (A23)$$

$$c_{jmq} = \langle\psi_{mq}^{(0)}|\tilde{t}\rangle|\chi_j^n\rangle|m\rangle. \qquad (A24)$$

As a matter of fact, those energy-increasing terms with $q = 17, 18, 19, 20$ (corresponding to the final states with both electrons at the orbits of the donor) and the cross-product terms with $\omega_{np,mq} \neq 0$ of Eq. (A23) do not contribute much to the chemical reaction probability. Therefore, a Fermi's golden-rule-like chemical reaction rate is obtained as

$$k_t = \frac{\pi J^2}{4Z\hbar}\sum_{m,n=0}^{\infty}\sum_{j=1}^{4}\sum_{p=21}^{24} e^{-\beta m\hbar\omega}|\langle n|e^{-2\phi(b^\dagger - b)}|m\rangle|^2 R_{jmnp}$$
$$(A25)$$

with the coefficients being listed in Table II.

Appendix B: Singlet and triplet states interconversion

For the system initially in the state

$$\tilde{\rho}(0) = \tilde{\rho}_v \otimes \tilde{\rho}_n \otimes \tilde{\rho}_t, \tag{B1}$$

the probability of the electrons converted to the singlet state at time t reads

$$
\begin{aligned}
P_{t \to s} &= \mathrm{Tr}_{v,n,e}\left[\tilde{\rho}_s e^{-i\tilde{H}t/\hbar} \tilde{\rho}(0) e^{i\tilde{H}t/\hbar}\right] \tag{B2}\\
&= \frac{1}{4Z} \sum_{m,n} \sum_{i,j} e^{-\beta m \hbar \omega} \\
&\quad \times \left|\langle \tilde{s}|\langle \chi_i^n|\langle n|e^{-i\tilde{H}t/\hbar}|m\rangle|\chi_j^n\rangle|\tilde{t}\rangle\right|^2 \tag{B3}
\end{aligned}
$$

The eigenfunction of $\tilde{H}$ is approximated to the first order as

$$|\psi_{mq}\rangle = |\psi_{mq}^{(0)}\rangle + \sum_{n=0}^{\infty} \sum_{p=1}^{24} \xi(m,n,q,p)|\psi_{np}^{(0)}\rangle \tag{B4}$$

with

$$\xi(m,n,q,p) = \frac{\langle \psi_{np}^{(0)}|\tilde{H}^{(1)}|\psi_{mq}^{(0)}\rangle}{E_{mq}^{(0)} - E_{np}^{(0)}}, \tag{B5}$$

while the eigen energy is obtained to the second order as

$$E_{mq} = E_{mq}^{(0)} + \sum_{n,p} \frac{|\langle \psi_{np}^{(0)}|\tilde{H}^{(1)}|\psi_{mq}^{(0)}\rangle|^2}{E_{mq}^{(0)} - E_{np}^{(0)}}. \tag{B6}$$

As a result, the time evolution operator is approximated as

$$e^{-i\tilde{H}t/\hbar} = \sum_{k=0}^{\infty} \sum_{q=1}^{24} e^{\pm iE_{kq}t/\hbar} |\psi_{kq}\rangle \langle \psi_{kq}|. \tag{B7}$$

Neglecting the the second-order terms, we obtain the conversion probability as

$$
\begin{aligned}
P_{t \to s} &= \frac{1}{4Z} \sum_{m=0}^{\infty} \sum_{j,k=1}^{4} e^{-\beta m \hbar \omega} \\
&\quad \times \left|\sum_{q=1}^{16} \langle \check{t}|\langle \chi_k^n|\varphi_q\rangle \langle \varphi_q|\chi_j^n\rangle|\check{s}\rangle e^{-iE_{mq}t/\hbar}\right|^2 \\
&= \frac{1}{4Z} \sum_{m=0}^{\infty} \sum_{j,k=1}^{4} e^{-\beta m \hbar \omega} |D_{mjk}|^2, \tag{B8}
\end{aligned}
$$

where the coefficients D_{mjk} are listed in Table III.

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